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Ab initio theory of linear and nonlinear optics of liquid crystals

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A new theory of linear and nonlinear optics of liquid crystals is presented. It is based on the *ab initio* macroscopic Lagrangian theory of Lax and Nelson [Phys. Rev. B **4**, 3694 (1971)] for anisotropic crystals and the dissipation function theory of Lam and Lax [Phys. Fluids **21**, 9 (1978)] for liquid crystals. The theory is completely deductive and the effects of internal excitations can be included in principle. In this paper the formalism is presented with application to nematic liquid crystals. Dielectric constants with frequency dependence are given. Within the electric dipole approximation an effective equation of motion for the director is derived. It agrees with that of Zel'dovich, Yabiryan, and Chilingaryan (Zh. Eksp. Teor. Fiz. **81**, 72 (1981) [Sov. Phys.—JETP **54**, 32 (1981)]). This equation describes the optically induced reorientation of the molecules. Flexoelectric constants depending on the optical frequency are presented. The flexoelectric effect in our case arises from the induced dipoles due to director gradients and should exist even in molecules without permanent dipoles or quadrupole moments. This physical mechanism differs from that proposed by Meyer [Phys. Rev. Lett. **22**, 918 (1969)] and by Prost and Marcerou [J. Phys. (Paris) **38**, 315 (1977)]. Dissipative effects are also discussed with the use of a dissipation function.

I. INTRODUCTION

Nonlinear optics of liquid crystals have been extensively studied.[1–6] They are important from both the basic and applied points of view. However, the complexity of the problem has caused all theoretical approaches[6–8] in this field to be largely phenomenological involving some *ad hoc* approximations.

Our present approach differs from the previous ones[6–8] in that the reversible processes are derived from an *ab initio* Lagrangian from which the equations of motion of the director, internal coordinates, and the electromagnetic field are *derived* deductively and consistently. Conversation laws are automatically satisfied. The theory is semimacroscopic.[9,10] The irreversible processes such as damping and viscosity are derived from a dissipation function.[11–13]

At optical frequencies the center-of-mass variable of the molecule cannot respond to the electric field and does not enter into the dynamics. The electrons follow the motion of the optical field easily while the director changes with time only slowly. These properties simplify the problem drastically and allow one to adiabatically eliminate the internal coordinates in favor of the director, resulting in an effective equation of motion for the director.

For simplicity, in this paper, the electric-dipole approximation is used and only two internal coordinates are retained. One is the director and the other corresponds to an internal excitation. The general case of many internal excitations can be obtained easily. In Sec. II the general formulation for molecular liquids is presented. Dissipation is omitted and deferred until Sec. VII. The case of liquid crystals is specified in Sec. III. The equations of motion are given in Sec. IV and dielectric constants are derived. In Sec. V an effective equation of motion for the director is obtained and compared to others.[6–8] Flexoelectric effects are discussed in Sec. VI. Section VIII concludes the paper with brief discussions.

II. GENERAL FORMULATION

A. The Lagrangian

When all dissipative effects are absent the Lagrangian describing the system of molecules and the electromagnetic field, in the continuum limit, is given by[9]

$$L = L_P + L_F + L_I \ , \tag{2.1}$$

where the nonrelativistic particle Lagrangian is given by

$$L_P = \int d\mathbf{X} \left\{ \frac{1}{2} \sum_{\alpha=1}^{N} \rho^{\alpha} [\dot{\mathbf{x}}^{\alpha}(\mathbf{X},t)]^2 - \rho^0 F(\mathbf{x}^{\beta}(\mathbf{X},t), \mathbf{x}^{\beta}_{,A}(\mathbf{X},t)) \right\} \tag{2.2}$$

and the electromagnetic-field–particle interaction Lagrangian is given by

$$L_I=\int d\mathbf{X}\sum_{\alpha=1}^{N} q^{\alpha}[\dot{\mathbf{x}}^{\alpha}(\mathbf{X},t)\cdot\mathbf{A}(\mathbf{x}^{\alpha}(\mathbf{X},t))-\Phi(\mathbf{x}^{\alpha}(\mathbf{X},t))]\ . \tag{2.3}$$

Here, $\mathbf{x}^{\alpha}$ represents the position of the αth particle in a spatial frame. N is the number of different particles, ions and electrons, in a primitive unit cell in the case of crystals,[9] and in a molecule in the case of molecular liquids[12] such as liquid crystals.[13] The quantity $\mathbf{X}$ is a continuum variable that designates or names a material point in the material frame and is a time-independent quantity. Both the spatial and material frames are chosen to be Cartesian for convenience. An overdot represents the material time derivative. ρ^{α} and q^{α} are, respectively, the mass and charge of the αth particle divided by the average volume occupied by a molecule. ρ^0 ($\equiv\sum\rho^{\alpha}$) is the mass density of the medium and $\rho^0 F$ the free energy per unit volume.[13]

The vector and scalar potentials $\mathbf{A}$ and Φ in the Lagrangian are the generalized coordinates describing the electromagnetic field. They are functions of position $\mathbf{z}$ in the spatial frame and are related to the electric field $\mathbf{E}$ and the magnetic induction $\mathbf{B}$ by

$$\mathbf{E}(\mathbf{z},t)\equiv-\nabla\Phi(\mathbf{z},t)-\frac{\partial\,\mathbf{A}(\mathbf{z},t)}{\partial t}\ , \tag{2.4}$$

$$\mathbf{B}(\mathbf{z},t)\equiv\nabla\times\mathbf{A}(\mathbf{z},t)\ . \tag{2.5}$$

In terms of $\mathbf{E}$ and $\mathbf{B}$, the field Lagrangian is given by

$$L_F=\int\tfrac{1}{2}\epsilon_0[\mathbf{E}^2(\mathbf{z},t)-c^2\mathbf{B}^2(\mathbf{z},t)]d\mathbf{z}\ , \tag{2.6}$$

where ϵ_0 is the permittivity of free space and c is the free-space velocity of light. Equations (2.1)–(2.6) are the basic equations of this theory. Note that the mks system of units is used.

Equation (2.3) is equivalent to

$$L_I=\int[\mathbf{j}(\mathbf{z},t)\cdot\mathbf{A}(\mathbf{z},t)-q(\mathbf{z},t)\Phi(\mathbf{z},t)]d\mathbf{z}\ , \tag{2.7}$$

where the charge and current densities are defined by

$$q(\mathbf{z},t)\equiv\sum_{\alpha=1}^{N} q^{\alpha}\int\delta(\mathbf{z}-\mathbf{x}^{\alpha}(\mathbf{X},t))d\mathbf{X}\ , \tag{2.8}$$

$$\mathbf{j}(\mathbf{z},t)\equiv\sum_{\alpha=1}^{N} q^{\alpha}\int\dot{\mathbf{x}}^{\alpha}(\mathbf{X},t)\delta(\mathbf{z}-\mathbf{x}^{\alpha}(\mathbf{X},t))d\mathbf{X}\ . \tag{2.9}$$

By Eqs. (2.6) and (2.7) one obtains the Lagrangian equations for Φ and A:

$$\epsilon_0\nabla\cdot\mathbf{E}=q\ , \tag{2.10}$$

$$\frac{1}{\mu_0}\nabla\times\mathbf{B}-\epsilon_0\frac{\partial\mathbf{E}}{\partial t}=\mathbf{j}\ , \tag{2.11}$$

where $\mu_0\equiv(c^2\epsilon_0)^{-1}$ is the permeability of free space. The other two of Maxwell's equations,

$$\nabla\times\mathbf{E}+\frac{\partial\mathbf{B}}{\partial t}=0\ , \tag{2.12}$$

$$\nabla\cdot\mathbf{B}=0\ , \tag{2.13}$$

follow directly from Eqs. (2.4) and (2.5).

B. Electric-dipole approximation

The charge and current densities can be expressed in a multipole expansion. In the absence of magnetic fields, the electric-dipole approximation in which the magnetic-dipole, electric-quadrupole, and higher-order terms are dropped is adequate. Furthermore, if any free charge is ignored one has[9]

$$q=-\nabla\cdot\mathbf{P}\ , \tag{2.14}$$

$$\mathbf{j}=\frac{\partial\mathbf{P}}{\partial t}+\nabla\times(\mathbf{P}\times\dot{\mathbf{x}})\ , \tag{2.15}$$

and

$$L_I=\int\mathbf{P}\cdot\mathbf{E}d\mathbf{z}\ , \tag{2.16}$$

where $\mathbf{P}$ is the polarization. In terms of a set of internal coordinates $\{\mathbf{y}^{\mu}(\mathbf{X},t)\}$, $\mu=1,\ldots,N-1$, one has

$$L_P=\int d\mathbf{X}\left[\tfrac{1}{2}\sum_{\mu=0}^{N-1} m^{\mu}(\dot{\mathbf{y}}^{\mu})^2-\rho^0 F\right]\ , \tag{2.17}$$

$$\mathbf{P}=\sum_{\mu=1}^{N-1} q^{\mu}\hat{\mathbf{y}}^{\mu}/\hat{J}\ , \tag{2.18}$$

where

$$\hat{\mathbf{y}}^{\mu}(\mathbf{z},t)=[\mathbf{y}^{\mu}(\mathbf{X},t)]_{\mathbf{x}(\mathbf{X},t)=\mathbf{z}},\quad \mu-1,\ldots,N-1 \tag{2.19}$$

$$\hat{J}(\mathbf{z},t)=[\det(x_{i,A})]_{\mathbf{x}(\mathbf{X},t)=\mathbf{z}}\ . \tag{2.20}$$

Note that the internal coordinates are chosen so that the set $\{\mathbf{x},\mathbf{y}^{\mu}\}$ retains the diagonality of the kinetic energy; $\mathbf{x}$ is the center-of-mass variable of the set of masses ρ^{α} and $\mathbf{x}\equiv\mathbf{y}^0$. In Eq. (2.20), $x_{i,A}\equiv\partial x_i/\partial X_A$ and q^{μ} is the charge density associated with $\mathbf{y}^{\mu}$.

III. LIQUID CRYSTALS

A. Basic assumptions

In this paper the liquid crystal is assumed to be incompressible. It follows that the Jacobian satisfies

$$\hat{J}=1\ . \tag{3.1}$$

We then assume that there are only two important internal coordinates, $\hat{\mathbf{y}}^1$ and $\hat{\mathbf{y}}^2$, with the identification,

$$\hat{\mathbf{y}}^1=l\mathbf{n},\quad \hat{\mathbf{y}}^2\equiv\mathbf{y}\ . \tag{3.2}$$

Here, $\mathbf{n}$ is the director.[14] The length l is assumed to be constant and

$$\mathbf{n}^2=1\ . \tag{3.3}$$

The q^{μ} charge for $\mu=1$ gives a permanent electric dipole along $\mathbf{n}$, which is unimportant in the optical regime. Therefore we set

$$q^{\mu}=0\quad\text{for }\mu=1\ . \tag{3.4}$$

For convenience we set $q^{\mu}\equiv-q$ for $\mu=2$. A simple three-particle model that satisfies these assumptions is presented in the Appendix. The model is used to motivate our assumptions here and provides the basis for order-of-magnitude estimations.

Since liquid crystals are fluids there exists no natural state as in the case of crystals. We therefore adopt the liquidlike hypothesis,[13] adding one internal vector coordinate **y**, and assume

$$F=F(\rho,n_i,n_{i,j},y_i),\quad i,j=1,2,3 \tag{3.5}$$

where ρ is the density and $n_{i,j}\equiv\partial n_i/\partial z_j$. Note that Eq. (3.1) implies that $\rho=\rho^0=\text{const}$.

B. Nematics

The usual nematic has local symmetry $D_{\infty h}$ with respect to the symmetry axis **n**. When expanded to second order, F with symmetry $D_{\infty h}$ is given by

$$\rho F=\tfrac{1}{2}a\mathbf{y}\cdot\mathbf{y}+\tfrac{1}{2}b(\mathbf{y}\cdot\mathbf{n})^2+F_0(n_i,n_{i,j}) , \tag{3.6}$$

where F_0 is the Oseen-Frank free-energy density given by

$$F_0=\tfrac{1}{2}K_1(\nabla\cdot\mathbf{n})^2+\tfrac{1}{2}K_2(\mathbf{n}\cdot\nabla\times\mathbf{n})^2+\tfrac{1}{2}K_3(\mathbf{n}\times\nabla\times\mathbf{n})^2 . \tag{3.7}$$

In Eq. (3.6) an additional term with y_i coupled to $n_{i,j}$ is omitted. It contributes to the flexoelectric effect[14] and is usually much smaller in magnitude. The latter will be discussed separately in Sec. VI. Higher-order terms may be added to Eq. (3.6) as needed. Nonlinear optical effects already exist in Eq. (3.6) (see Sec. IV).

Because of the positive-definite property of F, the constants a, b, K_1, K_2, and K_3 satisfy the inequalities

$$a>0,\quad a+b>0,\quad K_i>0,\quad i=1,2,3 . \tag{3.8}$$

IV. DIELECTRIC CONSTANTS

The equations of motion for **n** and **y** are given by the Lagrangian equations with the two constraints of Eqs. (3.1) and (3.3) included by the use of Lagrangian multipliers.[13] We then have

$$I\frac{\partial^2 n_i}{\partial t^2}=\lambda n_i-b(\mathbf{y}\cdot\mathbf{n})y_i+\frac{\partial}{\partial z_j}\frac{\partial F_0}{\partial n_{i,j}}-\frac{\partial F_0}{\partial n_i} , \tag{4.1}$$

$$m\frac{\partial^2}{\partial t^2}y_i=-ay_i-b(\mathbf{y}\cdot\mathbf{n})n_i-qE_i , \tag{4.2}$$

where λ is a Lagrangian multiplier, $I=Ml^2$, $m^\mu\equiv M$ for $\mu=1$, and $m^\mu\equiv m$ for $\mu=2$. Here M is comparable to the mass of ions and m to that of electrons.

Under the action of an oscillating field $E\sim\exp(-i\omega t)$ with optical angular frequency ω, it is an excellent approximation to allow **y** to adiabatically follow **n**. We therefore assume **n** is constant and $y\sim\exp(-i\omega t)$. Equation (4.2) becomes

$$(a-m\omega^2)\mathbf{y}+b(\mathbf{y}\cdot\mathbf{n})\mathbf{n}=-q\mathbf{E} , \tag{4.3}$$

which possesses the formal solution

$$\mathbf{y}=-q[(a+b-m\omega^2)^{-1}\mathbf{nn}+(a-m\omega^2)^{-1}(\mathbb{1}-\mathbf{nn})]\mathbf{E} . \tag{4.4}$$

Now, **n** can resume its slow time variation. Putting Eq. (4.4) into Eqs. (2.18), (3.2), and (3.4) we have

$$P_i=-qy_i\equiv\epsilon_0(\kappa_{ij}-\delta_{ij})E_j , \tag{4.5}$$

where the dielectric constant κ_{ij} is given by

$$\kappa_{ij}=\kappa_\perp\delta_{ij}+(\kappa_\parallel-\kappa_\perp)n_in_j \tag{4.6}$$

with

$$\kappa_\parallel\equiv1+(q^2/\epsilon_0)/(a+b-m\omega^2) , \tag{4.7}$$

$$\kappa_\perp\equiv1+(q^2/\epsilon_0)/(a-m\omega^2) . \tag{4.8}$$

The refractive indices n_0 and n_e are given by $n_0=(\kappa_\perp)^{1/2}$ and $n_e=(\kappa_\parallel)^{1/2}$, respectively.

Note that $b>0$ ($b<0$) implies $\kappa_a<0$ ($\kappa_a>0$) where $\kappa_a\equiv\kappa_\parallel-\kappa_\perp$. Since **n** is a function of **E**, **P** in Eq. (4.5) can be nonlinear in **E**. The results of Eqs. (4.7) and (4.8) are found[15] to be in agreement with experiments.[16]

V. OPTICAL REORIENTATION

Consider an electric field $\mathbf{E}(\mathbf{z},t)$ given by

$$\mathbf{E}=\tfrac{1}{2}[E^-(\mathbf{z})e^{-i\omega t}+\mathbf{E}^+(\mathbf{z})e^{i\omega t}] , \tag{5.1}$$

where $\mathbf{E}^-$ is the complex amplitude and $\mathbf{E}^+=(\mathbf{E}^-)^*$, the complex conjugate of $\mathbf{E}^-$. Since Eq. (4.2) is linear in **y** one can solve Eqs. (4.2) and (5.1) for y and obtain a solution similar to Eq. (4.4), viz.,

$$y_i^\pm=-\frac{\epsilon_0}{q}(\kappa_{ij}-\delta_{ij})E_j^\pm \tag{5.2}$$

with κ_{ij} given by Eqs. (4.6)–(4.8) and

$$\mathbf{y}=\tfrac{1}{2}(\mathbf{y}^-e^{-i\omega t}+\mathbf{y}^+e^{i\omega t}) , \tag{5.3}$$

where $\mathbf{y}^+=(\mathbf{y}^-)^*$.

Let us consider the b term in Eq. (4.1). By Eq. (5.2) we have

$$(\mathbf{y}\cdot\mathbf{n})\mathbf{y}=\tfrac{1}{4}[(\mathbf{y}^-\cdot\mathbf{n})\mathbf{y}^++(\mathbf{y}^+\cdot\mathbf{n})\mathbf{y}^-] , \tag{5.4}$$

where the terms with factor $\exp(+i2\omega t)$ are omitted. Putting Eq. (5.2) into Eq. (5.4) we have

$$(\mathbf{y}\cdot\mathbf{n})\mathbf{y}=\frac{1}{4}\left[\frac{\epsilon_0}{q}\right]^2(\kappa_\parallel-1)\times\{(\mathbf{n}\cdot\mathbf{E}^-)[(\kappa_\perp-1)\mathbf{E}^++\kappa_a\mathbf{n}(\mathbf{n}\cdot\mathbf{E}^+)]+\text{c.c.}\} . \tag{5.5}$$

In Eq. (5.5) the κ_a term is proportional to **n** which may be absorbed into the $\lambda\mathbf{n}$ term in Eq. (4.1) and can thus be dropped. Using Eqs. (4.7) and (4.8) we then have

$$b(\mathbf{y}\cdot\mathbf{n})\mathbf{y}=-\tfrac{1}{4}\epsilon_0\kappa_a[(\mathbf{n}\cdot\mathbf{E}^-)\mathbf{E}^++(\mathbf{n}\cdot\mathbf{E}^+)\mathbf{E}^-] . \tag{5.6}$$

The director orientation is then obtained by solving Eqs.

(4.1) and (5.6) together with the Maxwell equations coupled with Eq. (4.5).

To facilitate the comparison with other theories[6-8] we may rewrite Eqs. (4.1) and (5.6) as

$$I\frac{\partial^2 n_i}{\partial t^2}+\frac{\partial F_0}{\partial n_i}-\frac{\partial}{\partial z_j}\frac{\partial F_0}{\partial n_{i,j}}+\frac{\partial F_E}{\partial n_i}=\lambda n_i \ , \tag{5.7}$$

where

$$F_E \equiv -\tfrac{1}{4}\epsilon_0\kappa_a(\mathbf{n}\cdot\mathbf{E}^-)(\mathbf{n}\cdot\mathbf{E}^+) \ . \tag{5.8}$$

In the cgs system, F_E becomes

$$F_E=-\frac{\epsilon_a}{16\pi}(\mathbf{n}\cdot\mathbf{E}^-)(\mathbf{n}\cdot\mathbf{E}^+) \ , \tag{5.9}$$

where ϵ_a $(=\epsilon_\parallel-\epsilon_\perp)$ is the usual dielectric anisotropy.[14] Apart from the moment-of-inertia I term in Eq. (5.7), which was dropped by Zel'dovich, Yabiryan, and Chilingaryan,[8] and the dissipative term in Eq. (3) of Ref. 8, which is omitted by us here,[17] our director equation is formally the same as that of Zel'dovich, Yabiryan, and Chilingaryan, which was assumed on a somewhat *ad hoc* basis (see also Ref. 3).

In the other two approaches,[6,7] which are also *ad hoc* in nature, one finds

$$F_E=-\tilde{I}\tilde{n}/c \ , \tag{5.10}$$

where $\tilde{I}$ is the intensity of the incident field; $\tilde{n}=n_r$ was assumed by Durbin, Arakelian, and Shen,[7] and $\tilde{n}=n_p$ assumed by Ong.[6] Here c/n_r is the ray velocity and c/n_p is the phase velocity. The relationship of these two approaches to that of Zel'dovich, Yabiryan, and Chilingaryan has been elaborated by Ong[6] and by Tabiryan, Sukhov, and Zel'dovich.[3] We therefore refrain from further comments here.

VI. FLEXOELECTRIC CONSTANTS

On the rhs of Eq. (3.6) one may add the terms

$$F_1=c\mathbf{y}(\mathbf{n}\cdot\nabla)\mathbf{n}+d(\mathbf{y}\cdot\mathbf{n})(\nabla\cdot\mathbf{n}) \ , \tag{6.1}$$

where the constants c and d are positive. Eq. (4.2) then becomes

$$m\frac{\partial^2 y_i}{\partial t^2}=-ay_i-b(\mathbf{y}\cdot\mathbf{n})n_i-c(\mathbf{n}\cdot\nabla)n_i-dn_i(\nabla\cdot\mathbf{n})-qE_i \ . \tag{6.2}$$

Similar to Eq. (4.4) one obtains

$$\begin{aligned}\mathbf{y}=&-q[(a+b-m\omega^2)^{-1}\mathbf{nn}+(a-m\omega^2)^{-1}(\mathbb{1}-\mathbf{nn})]\mathbf{E}\\&-c(a-m\omega^2)^{-1}(\mathbf{n}\cdot\nabla)\mathbf{n}-d(a+b-m\omega^2)^{-1}(\nabla\cdot\mathbf{n})\mathbf{n} \ .\end{aligned} \tag{6.3}$$

The polarization is now given by

$$P_i=\epsilon_0(\kappa_{ij}-\delta_{ij})E_j+e_1n_i(\nabla\cdot\mathbf{n})+e_3(\mathbf{n}\cdot\nabla)n_i \ , \tag{6.4}$$

with κ_{ij} given by Eq. (4.6) and

$$e_1=dq/(a+b-m\omega^2) \ , \tag{6.5}$$

$$e_3=cq/(a-m\omega^2) \ . \tag{6.6}$$

Consequently, e_1 and $\kappa_\parallel$ have the same resonance frequency while e_3 and $\kappa_\perp$ share a different resonance frequency. Also, e_1 and e_3 are positive (negative) when the optical frequency is below (above) their respective resonance frequencies. This result should not be confused with those discussed by Dozov, Penchev, Martinot-Lagarde, and Durand[18] concerning the static case. At $\omega=0$, the permanent electric dipoles of the molecules ignored here will be important and our results have to be modified. However, Eqs. (6.5) and (6.6), the effect of which should still be present at $\omega=0$, are expected to be correct in the optical regime even when the molecules possess permanent dipoles.

The flexoelectric effects as exemplified in Eqs. (6.4)–(6.6) arise from the *induced* dipoles and should therefore exist even for molecules without permanent dipoles or quadrupole moments. In this regard it differs from the physical mechanism proposed by Meyer[19] (requiring permanent dipoles) and that by Prost and Marcerou[20] (requiring quadrupole moments).

VII. DISSIPATIVE EFFECTS

Dissipative effects may be described by the use of a dissipation function.[11-13] At constant temperature and requiring that the dissipation function D vanishes under rigid body motions, one should have

$$D=D(d_{ij},N_i,Y_i) \ , \tag{7.1}$$

where

$$\begin{aligned}d_{ij}&\equiv\tfrac{1}{2}(v_{i,j}+v_{j,i}) \ ,\\ N_i&\equiv\dot{n}_i=\tfrac{1}{2}(v_{i,j}-v_{j,i})n_j \ ,\\ Y_i&\equiv\dot{y}_i-\tfrac{1}{2}(v_{i,j}-v_{j,i})y_j \ .\end{aligned} \tag{7.2}$$

Equation (7.1) generalizes the case in Ref. 13 in which Y_i is absent. At optical frequency the molecular center-of-mass motion can be ignored, resulting in $D=D(N_i,Y_i)$.

For nematics, imposing $D_{\infty h}$ material symmetry we have

$$\rho D=\tfrac{1}{2}\gamma(\mathbf{N}\cdot\mathbf{N})+\tfrac{1}{2}\alpha(\mathbf{Y}\cdot\mathbf{n})^2+\tfrac{1}{2}\eta(\mathbf{Y}\cdot\mathbf{Y}) \ . \tag{7.3}$$

The equations of motion are now given by[13]

$$\frac{\delta L}{\delta y_i^\mu}=\frac{\delta\rho D}{\delta\dot{y}_i^\mu}, \quad \mu=0,1,2 \ . \tag{7.4}$$

To lowest order, $N_i\simeq\partial n_i/\partial t$ and $Y_i\simeq\partial y_i/\partial t$. To the rhs of Eqs. (4.1) and (5.7) one should add the term $-\gamma\partial n_i/\partial t$; to the rhs of Eqs. (4.2) and (6.2) there are the additional terms $-\alpha(\mathbf{n}\cdot\partial\mathbf{y}/\partial t)n_i-\eta\partial y_i/\partial t$. The results in the previous sections remain valid except that for everything $a\rightarrow a-i\omega\eta$ and $b\rightarrow b-i\omega\alpha$. In particular, $\kappa_\parallel$, $\kappa_\perp$, e_1, and e_3 become complex numbers and no longer diverge at the resonance frequencies.

VIII. CONCLUSION

An *ab initio* theory using Lagrangian and dissipation function describing the interaction of liquid crystals with electromagnetic fields is introduced. The Maxwell equations, the equations of motion of the director and an internal coordinate are derived. Frequency-dependent dielectric constants and flexoelectric constants in the optical regime are given for the first time. A new mechanism of flexoelectric effects is proposed. Our director equation agrees with that of Ref. 8.

Our theory generalizes that of Lax and Nelson[9] by including dissipative effects and by including the $n_{i,j}$ dependence in F. It generalizes that of Lam and Lax[11–13] by including one more internal coordinate **y** and the electromagnetic interactions.

The fact that the parallel and perpendicular components of the dielectric constant have the different resonance frequencies obtained in this paper is a special and somewhat artificial feature derived from the model used, viz., only two internal coordinates (**n** and **y**) are retained. In the more general case with more internal coordinates, both the parallel and perpendicular excitations are related to the normal modes[10] and will have identical resonance frequencies as observed experimentally.[21]

Although the motion of the center-of-mass variable is omitted here, it is straightforward to include it within our formalism. When this is done it is then possible to discuss the rich phenomena of acoustic properties. In the presence of magnetic fields the magnetic dipole terms have to be included.

Our formalism is equally applicable to dielectric liquids and ferrofluids.[22]

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APPENDIX: THE THREE-PARTICLE MODEL

Let us consider a model of a molecule consisting of three particles (Fig. 1), i.e., $N=3$. For convenience, in this appendix, α naming the particles in Sec. II will be written as subscripts instead of superscripts, e.g., $\mathbf{x}^\alpha \to \mathbf{x}_\alpha$. It is assumed that $\rho_1 \equiv m_1$, $\rho_2 \equiv m_2$, $\rho_3 \equiv \mu$, and $q_3 = -(q_1 + q_2)$.

The center of mass coordinate **x** is given by

$$\mathbf{x} = (m_1\mathbf{x}_1 + m_2\mathbf{x}_2 + \mu\mathbf{x}_3)/\rho_0 , \tag{A1}$$

where

$$\rho_0 = m_1 + m_2 + \mu . \tag{A2}$$

Define

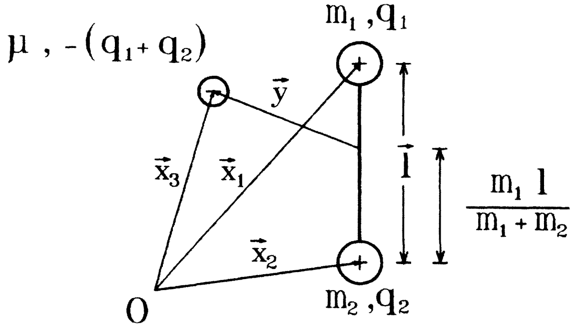

FIG. 1. The three-particle molecular model.

$$\begin{aligned} l &\equiv \mathbf{x}_1 - \mathbf{x}_2 , \\ \mathbf{y} &\equiv \mathbf{x}_3 - \left[\mathbf{x}_2 + \frac{m_1}{m_1+m_2} l \right] . \end{aligned} \tag{A3}$$

Equations (A1) and (A3) may be inverted to give

$$\begin{aligned} \mathbf{x}_1 &= \mathbf{x} - (\mu/\rho_0)\mathbf{y} + \frac{m_2}{m_1+m_2} l , \\ \mathbf{x}_2 &= \mathbf{x} - (\mu/\rho_0)\mathbf{y} - \frac{m_1}{m_1+m_2} l , \\ \mathbf{x}_3 &= \mathbf{x} + \frac{m_1+m_2}{\rho_0}\mathbf{y} . \end{aligned} \tag{A4}$$

It can be easily shown that the kinetic energy per unit volume

$$T \equiv \tfrac{1}{2} \sum_{\alpha=1}^{3} \rho_\alpha (\dot{\mathbf{x}}_\alpha)^2 \tag{A5}$$

$$= \tfrac{1}{2} \sum_{\mu=0}^{2} m_\mu (\dot{\mathbf{y}}_\mu)^2 \tag{A6}$$

with

$$\mathbf{y}_0 \equiv \mathbf{x}, \quad \mathbf{y}_1 \equiv l, \quad \mathbf{y}_2 \equiv \mathbf{y} ,$$

$$m_0 = \rho_0, \quad m_1 = m_1 m_2/(m_1+m_2), \quad m_3 = \mu/\rho_0 . \tag{A7}$$

In other words, $\{\mathbf{x}, \mathbf{l}, \mathbf{y}\}$ retain the diagonality of the kinetic energy and $\{\mathbf{l}, \mathbf{y}\}$ is a pair of internal coordinates.

The polarization is then given by

$$\begin{aligned} \mathbf{p}(\mathbf{X},t) &\equiv \sum_\alpha q_\alpha (\mathbf{x}_\alpha - \mathbf{x}) \\ &= -(q_1+q_2)\mathbf{y} + \frac{q_1 m_2 - q_2 m_1}{m_1+m_2} l . \end{aligned} \tag{A8}$$

Under the assumption that

$$q_1/q_2 = m_1/m_2 , \tag{A9}$$

we have

$$\mathbf{p} = -(q_1+q_2)\mathbf{y} . \tag{A10}$$

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